Supporting Information

Intermolecular 1,5-Dipolar Cycloaddition Reaction of Tungsten-Containing Vinyl-Azomethine Ylides Leading to Seven-Membered Heterocycles

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General. All operations were performed under an argon atmosphere or a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500 (500 MHz for ^1H and 125 MHz for ^{13}C), a JEOL AL-400 (400 MHz for ^1H and 100 MHz for ^{13}C), or a JEOL JNMLA-300 (300 MHz for ^1H and 75 MHz for ^{13}C) spectrometer in CDCl_3 (99.8% atom enriched, Acros Co., Ltd.) or CD_2Cl_2 . Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual CHCl_3 (δ_{H} 7.26) for ^1H spectra and CDCl_3 for ^{13}C (δ_{C} 77.0) spectra, or to residual CH_2Cl_2 (δ_{H} 5.32) for ^1H spectra and CD_2Cl_2 for ^{13}C (δ_{C} 53.2) spectra. IR spectra were recorded on an FT/IR-460 plus spectrometer (JASCO Co., Ltd.). High resolution mass analyses (FAB) were performed on a JEOL JMS-700 mass spectrometer using PEG 400, 3-nitrobenzyl alcohol, or 2-nitrophenyl octyl ether as matrix. Elemental analyses were performed on a Perkin-Elmer 2400 instrument. Photoirradiation was performed with a 250W super high-pressure mercury lamp having liquid light guide (USHIO INC.) otherwise noted. Silica Gel 60 (Kanto Chemical Co., Inc.) or Aluminum oxide 90 active neutral (activity I) (0.063-0.200 mm, Merck) was used for flash column chromatography. Merck Kieselgel 60 F₂₅₄ (0.25 mm thickness, coated on glass 20×20 cm²) plate was used for thin layer chromatography (TLC), and Wakogel[®] B-5F coated on glass in a thickness of 0.7 mm was used for preparative TLC. THF was freshly distilled from benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over Molecular Sieves. Tungsten hexacarbonyl was purchased from Soekawa Chemical Co., Ltd.

General Experimental Procedures

General procedure for the preparation of aldimines (1a, b) derived from 2-(1-alkynyl)anilines (15, 16) and benzaldehyde:

***o*-(but-3-en-1-ynyl)aniline (15)**

To a mixture of *o*-ethynylaniline **14** (351 mg, 3.0 mM), tetrakis(triphenylphosphine)palladium(0) (34.9 mg, 0.01 mM) and copper(I) iodide (19.3 mg, 0.03 mM) in triethylamine (6.0 ml) and DMF (1.5 ml) was added vinyl bromide (0.85 ml) at room temperature and the mixture was stirred overnight. The reaction was quenched with saturated NH₄Cl aq. The aqueous layer was extracted with ether three times and the combined extracts were washed with brine, dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give aniline **15** (367mg, 2.56 mM) in 84% yield as orange oil.

IR (neat): 3474, 3380, 2212, 1614, 1491, 1456 cm⁻¹;

¹H-NMR (CDCl₃) (400 MHz): δ = 4.15-4.35 (brs, 2H), 5.55 (d, J = 11.2 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 6.10 (dd, J = 17.6, 11.2 Hz, 1H), 6.69-6.73 (m, 2H), 7.14 (dd, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H);

¹³C-NMR (CDCl₃) (100 MHz): δ = 86.5, 93.3, 107.6, 114.1, 117.0, 117.7, 126.2, 129.6, 132.0, 147.6;

HRMS (PEG 400): Calcd for C₁₀H₉N, M 143.0735. Found m/z 143.0763.

***(E)*-N-benzylidene-2-(but-3-en-1-ynyl)aniline (1a)**

To a stirred mixture of aniline **15** (1.05 g, 7.32 mM) and MS5A (10 g) in toluene (25 ml) was added benzaldehyde (0.82 ml, 8.07 mM) at room temperature. The reaction mixture was refluxed for 6 h and stirred for 27 h at ambient temperature, then filtered through a short pad of Celite[®], and the solvent was removed under reduced pressure to give imine **1a** quantitatively. To the residue, a small amount of BHT and dried MS4A were added and the crude product was purified by bulb-to-bulb distillation (145-155 °C / 0.035 mmHg) to give pure imine **1a** (1.47 g, 6.37 mM, 87%) as yellow oil.

IR (neat) 3062, 2202, 1702, 1631 cm⁻¹;

¹H-NMR (CDCl₃) (300 MHz): δ = 5.46 (dd, J = 11.0, 2.2 Hz, 1H), 5.62 (dd, J = 17.6, 2.2 Hz, 1H), 5.98 (dd, J = 17.6, 11.0 Hz 1H), 7.05 (dd, J = 7.9, 1.2 Hz, 1H), 7.15 (ddd, J = 7.9, 7.9, 1.2 Hz, 1H), 7.33 (ddd, J = 7.9, 7.9, 1.2 Hz, 1H), 7.48-7.54 (m, 4H), 7.91-7.97 (m, 2H), 8.48 (s, 1H);

¹³C NMR (CDCl₃) (100 MHz): δ = 87.7, 92.3, 116.0, 117.3, 119.5, 125.0, 126.5, 128.7, 128.9, 129.2, 131.5, 132.8, 136.0, 153.7, 161.9;

Anal. Calcd for C₁₇H₁₃N: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.00; H, 5.90; N, 5.78.

***o*-[(*E*)-pent-3-en-1-ynyl]aniline (16)**

Coupling of *o*-ethynylaniline (**14**, 1.13 g, 9.6 mM) and (*E*)-1-bromoprop-1-ene (1.7 ml, 19.7 mM) using tetrakis(triphenylphosphine)palladium(0) (137.3 mg, 0.119 mM) and copper(I) iodide (34.0 mg, 0.179 mM) was carried out according to the same procedure as that for the synthesis of **15** to give **16** (1.31 g, 8.35 mM, 87%) as orange oil.

IR (neat): 3473, 3378, 2189, 1613, 1490, 1455 cm⁻¹;

¹H-NMR (CDCl₃) (400 MHz): δ = 1.85 (d, J = 6.8 Hz, 3H), 4.11-4.25 (brs, 2H), 5.78 (d, J = 16.0

Hz, 1H), 6.24 (dq, $J = 16.0, 6.8$ Hz, 1H), 6.67 (m, 2H), 7.10 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H);

^{13}C -NMR (CDCl_3) (100 MHz): $\delta = 18.7, 84.0, 93.4, 108.3, 110.7, 114.1, 117.7, 129.2, 131.8, 139.3, 147.4$;

Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.78; H, 7.06; N, 8.67.

(*E*)-*N*-benzylidene-2-[(*E*)-pent-3-en-1-ynyl]aniline (1b**)**

Reaction of aniline **16** (604 mg, 3.84 mM) with bezaldehyde (0.45 ml, 4.4 mM) was carried out according to the same procedure as that for the synthesis of **1a**. Reaction proceeded quantitatively. Pure imine **1b** (740 mg, 3.01 mM, 75%) was obtained by bulb-to-bulb distillation (140-155°C / 0.003 mmHg).

IR (neat) :3025, 2196, 1701, 1633 cm^{-1} ;

^1H -NMR (CDCl_3) (300 MHz): $\delta = 1.78$ (dd, $J = 6.8, 1.7$, 3H), 5.67 (dq, $J = 15.6, 1.7$ Hz, 1H), 6.13 (dq, $J = 15.6, 6.8$ Hz, 1H), 7.03 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.13 (ddd, $J = 7.8, 7.8, 1.3$ Hz, 1H), 7.30 (ddd, $J = 7.8, 7.8, 1.3$ Hz, 1H), 7.44-7.52 (m, 4H), 7.91-7.97 (m, 2H), 8.48 (s, 1H);

^{13}C NMR (CDCl_3) (100 MHz): $\delta = 18.8, 85.4, 92.5, 111.0, 116.5, 119.5, 125.0, 128.6, 128.7, 128.9, 131.4, 132.7, 136.1, 139.5, 153.5, 161.8$;

Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.89; H, 6.14; N, 5.57.

Procedure for the tungsten-catalyzed reaction of imine derivative **1a with ketene silyl acetal **4** in the presence of triethylamine (Scheme 2):**

To a mixture of imine **1a** (37.9 mg, 0.164 mM), isopropyl triisopropylsilyl ketene acetal **4** (85.9 mg, 0.332 mM), MS4A (0.6 g) and tungsten hexacarbonyl (5.1 mg, 0.015 mM) in toluene (3.0 ml) was added triethylamine (20 μl , 0.15 mM), and the mixture was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) at ambient temperature. After 24 h, the reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed under reduced pressure. 0.1 M HCl aq. (1.5 ml), isopropyl alcohol (3.0 ml) and ethyl acetate (3.0 ml) were added and the mixture was stirred for 3 h. Then, pH 7 phosphate buffer was added and the products were extracted with ethyl acetate. Organic layer was dried with MgSO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel preparative TLC (hexane:ethyl acetate = 8:1) to give tricyclic enone **6a** (31.6 mg, 0.116 mM, 71%).

The reaction with stoichiometric amount of tungsten hexacarbonyl was also carried out according to the procedure described above.

6-phenyl-6,7-dihydroazepino[1,2-*a*]indol-8-one (6a**)**

IR (neat); 3060, 1652, 1605 cm^{-1} ;

¹H NMR (CDCl₃) (500 MHz): δ = 3.51 (dd, J = 15.6, 3.0 Hz, 1H), 3.65 (ddd, J = 15.6, 5.9, 2.0 Hz, 1H), 5.91 (dd, J = 12.2, 2.0 Hz, 2H), 6.06 (dd, J = 5.9, 3.0 Hz, 1H), 6.73-6.75 (m, 2H), 7.00 (s, 1H), 7.15-7.21 (m, 5H), 7.28-7.31 (m, 2H), 7.71 (ddd, J = 8.0, 0.8, 0.8 Hz, 1H).

¹³C NMR (CDCl₃) (125 MHz): δ = 47.8, 53.4, 109.8, 113.0, 121.0, 122.2, 125.3, 125.4, 125.5, 126.9, 127.7, 128.8, 133.0, 135.8, 137.7, 139.6, 197.6;

Anal. Calcd for C₁₉H₁₅NO: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.78; H, 5.75; N, 4.83.

General procedure for the tungsten-catalyzed reaction of imine derivative 1a with ketene silyl acetal having methyl or methoxy substituent in the presence of triethylamine (Table 1, entries 3 and 4):

To a mixture of a ketene silyl acetal (0.67-0.68 mM), MS4A (0.6 g), triethylamine (0.015 or 0.03 mM) and tungsten hexacarbonyl (0.013 mM) was slowly added an imine **1a** (0.13 mM) in toluene (0.25 ml) under irradiation over 6 to 7.5 h at room temperature (cooled with water bath), and the reaction mixture was further irradiated for a few hours. The reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed under reduced pressure. 0.1 M HCl aq. (1.5 ml), isopropyl alcohol (3.0 ml), and ethyl acetate (3.0 ml) were added and the mixture was stirred for 3 h. Then, pH 7 phosphate buffer was added and the products were extracted with ethyl acetate. Organic layer was dried with MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by silica-gel preparative TLC (hexane:ethyl acetate = 8:1) to give **6** as a diastereomer mixture (R¹ = H, R² = Me or MeO).

7-methyl-6-phenyl-6,7-dihydroazepino[1,2-*a*]indol-8-one (6**, R¹ = H, R² = Me)**

(major : minor = 57 : 43)

(major diastereomer, stereochemistry is not determined)

IR (neat); 3060, 2981, 2934, 1659, 1605 cm⁻¹;

¹H NMR (CDCl₃) (500 MHz): δ = 1.43 (d, J = 7.1 Hz, 3H), 3.70 (qd, J = 7.1, 2.9 Hz, 1H), 5.65 (d, J = 2.9 Hz, 1H), 6.10 (d, J = 12.2 Hz, 1H), 6.95 (s, 1H), 7.02-7.07 (m, 2H), 7.08-7.15 (m, 1H), 7.16-7.30 (m, 6H), 7.64 (d, J = 7.8 Hz, 1H).

¹³C NMR (CDCl₃) (125 MHz): δ = 14.8, 49.3, 62.1, 110.0, 112.8, 120.9, 122.0, 125.1, 125.6, 127.0, 127.1, 128.1, 128.6, 132.1, 135.6, 136.5, 139.1, 199.1;

Anal. Calcd for C₂₀H₁₇NO: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.79; H, 6.23; N, 4.60.

(minor diastereomer, stereochemistry is not determined)

IR (neat); 3061, 2971, 1651, 1605, 1452, 1427 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 1.26 (d, J = 7.3 Hz, 3H), 3.74 (qdd, J = 7.3, 5.2, 1.8 Hz, 1H), 5.80 (d, J = 5.2 Hz, 1H), 5.81 (dd, J = 12.2, 1.8 Hz, 1H), 6.73-6.77 (m, 2H), 7.01 (s, 1H), 7.13-7.22

(m, 5H), 7.30-7.34 (m, 2H), 7.72 (m, 1H).

¹³C NMR (CDCl₃) (125 MHz): δ = 15.5, 51.6, 58.8, 109.7, 112.6, 121.0, 122.1, 123.7, 125.3, 125.5, 127.2, 127.7, 128.8, 132.4, 136.2, 138.2, 140.6, 201.7;

Anal. Calcd for C₂₀H₁₇NO: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.30; H, 6.17; N, 4.58.

7-methoxy-6-phenyl-6,7-dihydroazepino[1,2-a]indol-8-one (major-6, R¹ = H, R² = MeO)

(major : minor = 57 : 43)

(major diastereomer, stereochemistry is not determined)

IR (neat); 3060, 2925, 1671, 1604 cm⁻¹;

¹H NMR (CDCl₃) (500 MHz): δ = 3.68 (s, 3H), 4.70 (d, J = 2.6 Hz, 1H), 5.86 (d, J = 12.5 Hz, 1H), 6.09 (d, J = 2.6 Hz, 1H), 6.85-6.89 (m, 2H), 7.01 (s, 1H), 7.14-7.22 (m, 5H), 7.30-7.36 (m, 2H), 7.71 (d, J = 8.1 Hz, 1H).

¹³C NMR (CDCl₃) (125 MHz): δ = 58.2, 59.5, 87.7, 109.9, 113.1, 121.3, 122.1, 122.2, 125.5, 126.0, 127.0, 128.0, 128.5, 132.2, 135.0, 135.5, 139.2, 195.3;

HRSM (2-nitrophenyl octyl ether): Calcd for C₂₀H₁₈NO₂, [M+H] 304.1338. Found m/z 304.1320.

(minor diastereomer, stereochemistry is not determined)

IR (neat); 3060, 1652, 1605 cm⁻¹;

¹H NMR (CDCl₃) (500 MHz): δ = 3.41 (s, 3H), 4.43 (dd, J = 6.0, 2.0 Hz, 1H), 5.87 (dd, J = 12.2, 2.0 Hz, 1H), 6.12 (d, J = 6.0 Hz, 1H), 6.86-6.90 (m, 2H), 7.01 (s, 1H), 7.13 (ddd, J = 8.0, 8.0, 1.6 Hz, 1H), 7.18-7.29 (m, 6H), 7.68 (d, J = 8.0 Hz, 1H).

¹³C NMR (CDCl₃) (125 MHz): δ = 58.1, 58.6, 87.5, 109.9, 113.6, 121.0, 121.5, 122.2, 125.4, 125.8, 127.1, 128.3, 129.0, 133.9, 135.1, 136.5, 140.5, 197.6;

HRSM (3-nitrobenzyl alcohol): Calcd for C₂₀H₁₇NO₂, M 303.1259. Found m/z 303.1263.

Procedure for the tungsten-catalyzed reaction of imine derivative 1a with cyclic ketene acetal 7 in the presence of triethylamine (Table 1, entry 6):

To a mixture of imine **1a** (30.0 mg, 0.13 mM), cyclic ketene acetal **7** (51.7 mg, 0.60 mM), MS4A (0.6 g) and tungsten hexacarbonyl (51.8 mg, 0.15 mM) in toluene (3.0 ml) was added triethylamine (20 μ l, 0.15 mM), and the mixture was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) at ambient temperature. After 4.5 h, the reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography (hexane:ethyl acetate = 15:1) to give dioxolane-protected tricyclic indole **8** (31.4 mg, 0.099 mM, 76%).

9-ethenyl-3-phenyl-2,3-dihydropyrrolo[1,2-*a*]indol-1-spiro-2'-(1',3'-dioxacyclopentane) (8)

IR (neat); 3050, 2889, 1630, 1435 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 2.75 (dd, J = 13.6, 6.1 Hz, 1H), 3.21 (dd, J = 13.6, 7.9 Hz, 1H), 4.06-4.16 (m, 2H), 4.22-4.31 (m, 2H), 5.28 (dd, J = 11.6, 1.6 Hz, 1H), 5.48 (dd, J = 7.9, 6.1 Hz, 1H), 5.79 (dd, J = 7.6, 1.6 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.97-7.04 (m, 2H), 7.14 (dd, J = 8.0, 8.0 Hz, 1H), 7.23-7.35 (m, 5H), 7.92 (d, J = 8.0 Hz, 1H);

^{13}C NMR (CDCl_3) (100 MHz): δ = 51.1, 58.8, 65.3, 65.6, 107.1, 110.2, 110.9, 112.2, 120.4, 121.3, 122.0, 126.6, 127.9, 128.1, 128.8, 130.6, 132.4, 139.3, 139.9;

Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.18; H, 6.26; N, 4.15.

Procedure for the tungsten-catalyzed reaction of imine derivative 1b with ketene acetal in the presence of triethylamine (Table 1, entries 8):

To a mixture of imine **1b** (36.3 mg, 0.148 mM), ketene diisopropyl acetal (109 mg, 0.752 mM), MS4A (0.6 g) and tungsten hexacarbonyl (11.2 mg, 0.0318 mM) in toluene (3.0 ml) was added triethylamine (4.0 μl , 0.030 mmol), and the mixture was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) at 10 $^\circ\text{C}$. After 8 h, the reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed under reduced pressure. 0.1 M HCl aq. (1.5 ml), isopropyl alcohol (3.0 ml) and ethyl acetate (3.0 ml) were added and the mixture was stirred for 3 h. Then, pH 7 phosphate buffer was added and the products were extracted with ethyl acetate. Organic layer was dried with MgSO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel preparative TLC (hexane:ethyl acetate = 8:1) to give **6** and **8** as a mixture (35.4 mg).

The results of entries 1, 2, 7 and 9 in Table 1 were also obtained according to the procedure described above.

9-methyl-6-phenyl-6,7-dihydroazepino[1,2-*a*]indol-8-one (6, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$)

IR (neat); 3060, 2919, 1651, 1621, 1608 cm^{-1} ;

^1H NMR (CDCl_3) (500 MHz): δ = 1.90 (d, J = 1.1 Hz, 3H), 3.51 (dd, J = 15.1, 2.9 Hz, 1H), 3.65 (dd, J = 15.1, 6.0 Hz, 1H), 6.00 (dd, J = 6.0, 2.9 Hz, 1H), 6.75-6.79 (m, 2H), 6.89 (s, 1H), 7.13-7.21 (m, 5H), 7.23-7.28 (m, 2H), 7.68 (d, J = 8.0 Hz, 1H);

^{13}C NMR (CDCl_3) (125 MHz): δ = 19.6, 48.1, 53.8, 109.7, 111.4, 120.8, 121.7, 124.5, 125.5, 127.1, 127.6, 128.8, 130.9, 132.6, 136.0, 137.8, 139.0, 196.9;

Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{NO}$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.30; H, 6.21; N, 4.60.

(*E*)-3-phenyl-9-(prop-1-enyl)-2,3-dihydropyrrolo[1,2-*a*]indol-1-one (8, R¹ = Me, R² = H)

IR (neat); 2925, 1702, 1541 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 2.03 (d, J = 5.4 Hz, 3H), 3.07 (dd, J = 18.3, 4.0 Hz, 1H), 3.68 (dd, J = 18.3, 8.3 Hz, 1H), 5.70 (dd, J = 8.3, 4.0 Hz, 1H), 6.85-6.89 (m, 1H), 6.92-7.07 (m, 2H), 7.12-7.22 (m, 4H), 7.32-7.38 (m, 3H), 7.92-7.96 (m, 1H);

¹³C NMR (CDCl₃) (100 MHz): δ = 19.5, 50.6, 57.0, 111.6, 115.3, 121.0, 121.2, 122.9, 125.6, 126.0, 128.4, 129.2, 130.0, 130.3, 132.0, 134.7, 140.0, 191.3;

Anal. Calcd for C₂₀H₁₇NO: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.29; H, 5.88; N, 4.64.

Procedure for the tungsten-catalyzed reaction of imine derivative 1a with imine 9:

A mixture of imine **1a** (31.8 mg, 0.137 mM), imine **9** (63.9 mg, 0.536 mM), MS4A (0.6 g) and tungsten hexacarbonyl (5.5 mg, 0.016 mM) in toluene (0.25 ml) was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) having the collimator lens at ambient temperature. After disappearance of the starting material, the reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (hexane : ethyl acetate = 8:1 and toluene) to remove excess imine **9**. Then, the product was further purified by silica-gel preparative TLC (hexane:ethyl acetate = 8:1-1:5) to give **10** (34.5 mg, 0.0984 mM, 72%)

2-methyl-1,3-diphenyl-2,3-dihydro-1*H*-[1,3]diazepino[1,7-*a*]indole (10)

IR (neat); 3060, 3029, 1646, 1602, 1495, 1452 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 2.26 (s, 3H), 4.78 (dd, J = 3.2, 2.2 Hz, 1H), 5.88 (dd, J = 12.0, 2.2 Hz, 1H), 6.61 (s, 1H), 6.71 (s, 1H), 6.71 (dd, J = 12.0, 3.2 Hz, 1H), 7.01-7.08 (m, 3H), 7.13 (d, J = 7.2, 2H), 7.18-7.34 (m, 8H), 7.56-7.61 (m, 1H);

¹³C NMR (CDCl₃) (100 MHz): δ = 34.3, 59.9, 78.6, 105.9, 109.4, 119.9, 120.7, 122.3, 122.7, 126.8, 127.0, 127.9, 128.1, 128.1, 128.2, 128.7, 128.8, 137.9, 138.1, 139.8, 141.1.

Anal. Calcd for C₂₅H₂₂N₂O: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.38; H, 6.18; N, 8.07.

Procedure for the tungsten-catalyzed intramolecular cyclization reaction of imine derivative 11:

Preparation of 11

Reaction of aniline **14** (568.5 mg, 4.0 mM) and cinnamaldehyde (0.55 ml, 4.4 mM) was carried out according to the same procedure as that for the synthesis of **1a**, **b** to give **11** in 30% yield (303.6 mg, 1.18 mM) as orange oil (145-155°C / 0.035 mmHg).

(*E*)-2-(but-3-en-1-ynyl)-*N*-((*E*)-3-phenylprop-2-enylidene)aniline (**11**)

IR (neat) 3060, 1676, 1627, 1605 cm⁻¹;

¹H-NMR (CDCl₃) (300 MHz): δ = 5.50 (dd, *J* = 11.2, 2.2 Hz, 1H), 5.70 (dd, *J* = 17.5, 2.2 Hz, 1H), 6.03 (dd, *J* = 17.5, 11.2, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 7.11-7.19 (m, 3H), 7.29-7.44 (m, 4H), 7.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.7 Hz, 2H), 8.26 (dd, *J* = 5.6, 2.7 Hz, 1H);

¹³C NMR (CDCl₃) (75 MHz): δ = 87.7, 92.3, 116.2, 117.3, 119.4, 125.1, 126.6, 127.5, 128.5, 128.8, 129.2, 129.6, 133.0, 135.4, 144.4, 153.4, 163.4;

Anal. Calcd for C₁₉H₁₅N: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.41; H, 6.06; N, 5.28.

Procedure for the tungsten-catalyzed intramolecular cyclization reaction of imine derivative **11**:

A mixture of imine **11** (38.6 mg, 0.15 mM), triethylamine (20 μ l, 0.15 mM), MS4A (0.6 g) and tungsten hexacarbonyl (5.3 mg, 0.015 mM) in toluene (3.0 ml) was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) at ambient temperature. After disappearance of the starting material, the reaction mixture was filtered through a short pad of Celite[®] and the solvent was removed. The residue was purified by silica-gel column chromatography (hexane : ethyl acetate = 8:1 and toluene) to give **13** in 84% yield (19.4 mg, 0.0754 mM).

8-phenyl-8*H*-azepino[1,2-*a*]indole (**13**)

IR (neat) 3060, 1682, 1661, 1456, 1429 cm⁻¹;

¹H-NMR (CDCl₃) (500 MHz): δ = 4.45-4.48 (m, 1H), 5.18 (ddd, *J* = 9.7, 5.5, 1.4 Hz, 1H), 5.79 (ddd, *J* = 11.8, 5.2, 1.4 Hz, 1H), 6.51 (dd, *J* = 11.8, 1.4 Hz, 1H), 6.57 (s, 1H), 6.99 (dd, *J* = 9.7, 1.4 Hz, 1H), 7.18 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.24-7.30 (m, 2H), 7.32-7.36 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H);

¹³C NMR (CDCl₃) (125 MHz): δ = 46.4, 107.2, 109.4, 113.4, 119.7, 120.8, 121.2, 122.1, 123.0, 126.8, 127.8, 128.1, 128.9, 131.0, 136.9, 137.8, 144.5;

Anal. Calcd for C₁₉H₁₅N: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.47; H, 6.02; N, 5.17.